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OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 11/15/00	3. REPORT TYPE AND DATES COVERED Final Report, August 1996 - May 2000
4. TITLE AND SUBTITLE Three Dimensional Self-Assembled Electronic Nanostructures and Materials from Molecular Precursors		5. FUNDING NUMBERS DAAH04-96-1-0180	
6. AUTHOR(S) Thomas E. Mallouk			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Pennsylvania State University University Park, PA 16802		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER  ARO 35697.8 - PH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12 a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  This work developed chemical self-assembly methods for the fabrication of high dielectric oxide thin films and nanometer-scale electronic devices. The experimental emphasis was on preparation and testing of thin film dielectrics for memories, fabrication of single electron transistors, nucleation/growth of colloidal crystals, template synthesis of metal nanowires, and synthesis/combinatorial selection of alloy nanocrystals for chemical sensor applications. The thin film assemblies were deposited chemically from building blocks with characteristic dimensions of nanometers to microns: lamellar inorganic dielectrics, sol-gel metal oxide monolayers, polymer chains, colloidal metal and semiconductor particles, and nanowires. Thin films were grown by colloid adsorption, and by sol-gel processing of molecular precursors. Understanding and controlling self-assembly in these systems required theoretical development and computer simulations. Much of the theoretical effort was devoted to issues of simulation and visualization of particle self-assembly in one and two dimensions. Dynamical lattice gas models were developed, in order to model the assembly of mesoscopic particles. Two important successes of this project were (1) development of methods for making patterned, high dielectric thin film oxides by combining microcontact printing with inorganic self assembly, and (2) development of a combinatorial technique for identifying highly active alloy nanoparticle catalysts for amperometric sensors.			
14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT  UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)  
Prescribed by ANSI Std. Z39-18  
298-102

DTIC QUALITY IMPROVED 4  
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***Three Dimensional Self-Assembled Electronic Nanostructures and Materials from Molecular Precursors***

Thomas E. Mallouk

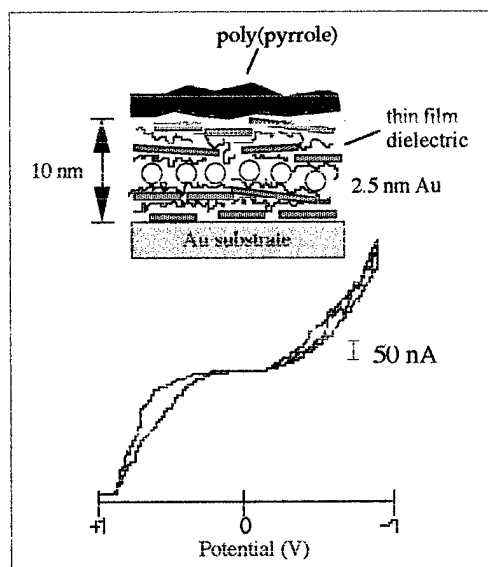
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**Problems Studied**

This project developed self-assembly techniques for electronic devices and materials, focusing particularly on nanoscale inorganic particles as building blocks of thin films. One of the motivations for this work was to find novel ways to make thin films of high dielectric materials for use in DRAM capacitors and related devices. Lamellar colloids were made by chemical exfoliation of layered titanates, tantalates, and niobates, and were grown layer by layer on surfaces by using wet chemical techniques. The condensation of these lamellar colloids into continuous films was studied, as was the preparation of continuous films from sol-gel precursors. The dielectric properties of the lamellar solids and films was studied, revealing some new low loss, high dielectric materials. Layered Coulomb blockade devices were prepared by similar methods and characterized. Nanoscale wires were also made by template electrochemical replication and initial studies of their self-assembly on surfaces were conducted. Finally, a method was developed for combinatorial discovery and optimization of new electrode materials for amperometric chemical and biochemical sensors.

**Summary of Most Important Results**

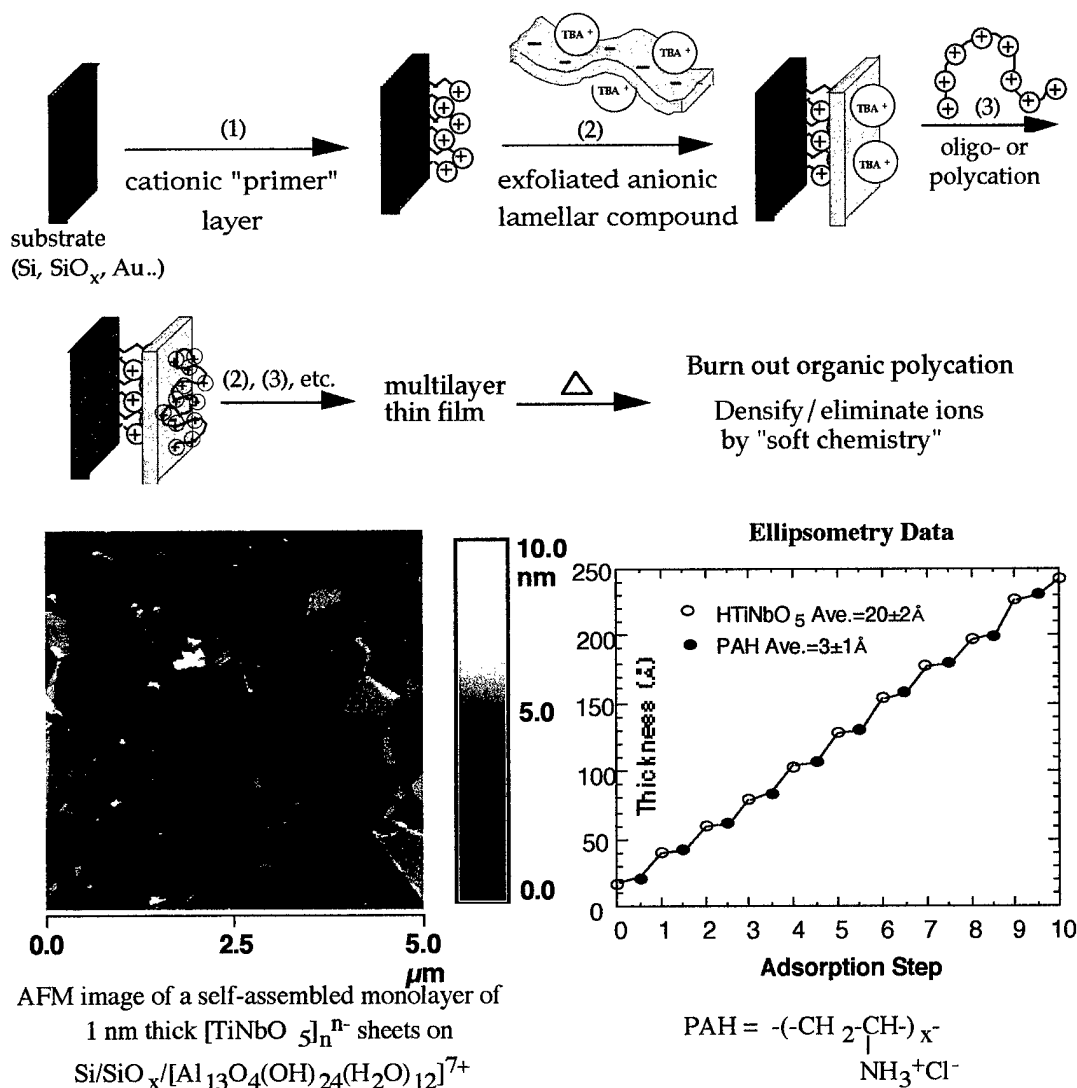
*Self-assembled Coulomb blockade devices.* Metal-insulator-nanoparticle-insulator-metal (MINIM) devices were prepared by self-assembly, from colloids of lamellar insulators, gold particles, and polymers. With sufficiently thin insulator layers (30-90 Å) a Coulomb gap is observed in the *i*-*V* characteristic. This behavior arises from single electron charging of the gold nanoparticles. The most remarkable feature of these devices is that there is an insignificant density of short circuits in a 1 cm<sup>2</sup> array containing approximately 10<sup>11</sup> parallel



**Figure 1.** Structure of a Coulomb blockade device made by layer-by-layer adsorption of insulator colloids and metal nanoparticle layers. The colloidal sheets are made by exfoliation of lamellar solids ( $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O or HTiNbO<sub>5</sub>). The top contact is also grown chemically, from by oxidation of pyrrole vapor.

tunnel junctions, despite the fact that they are made entirely by "benchtop" chemical techniques. Angle-resolved XPS experiments confirm the lamellar structure of these devices. Figure 1 shows a cartoon of the structure as determined by XPS, and the i-V characteristics of a room temperature device made from 2.5 nm Au nanoparticles.

Theory predicts, and experimental data confirm, the dependence of the size of the Coulomb gap on temperature, insulator thickness, and nanoparticle diameter. The temperature dependence of the i-V behavior is currently being studied as a function of insulator and nanoparticle dimensions. Theoretical calculations by Korotkov and Likharev suggest that the i-V characteristics of Coulomb blockade devices should be improved by using "staircase" barriers, which consist of insulators of different barrier heights. We are currently



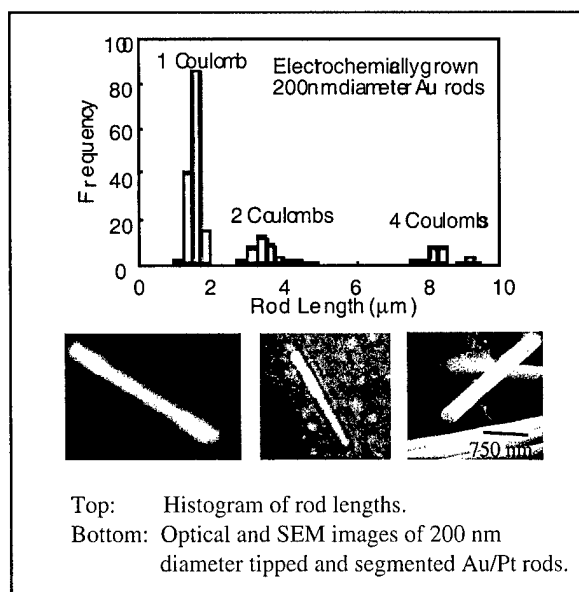
**Figure 2.** Top: Reaction scheme for layer-by-layer growth of high dielectric oxide films from lamellar colloids. Bottom: AFM image of the tiling of a surface by 1 nm thick HTiNbO<sub>5</sub> sheets, and ellipsometric thickness plot for layer-by-layer film growth.

investigating this possibility using insulator and metal nanoparticle layers grown sequentially as segments of metal nanorods in porous membranes (see below).

*Layer-by-layer assembly of high dielectric oxide thin films.* Representative high dielectric lamellar solids (in particular layer perovskite titanates, niobates, and tantalates) were grown as monolayer (1-2 nm) and multilayer thin films by ionic self-assembly. The dielectric properties of the lamellar solids and their condensation products were studied by complex impedance techniques. In bulk form, several of these materials have low-frequency dielectric constants in the 100-200 range; most exhibit high loss and decreasing dielectric constant at MHz and higher frequencies. However, a few, particularly acid-exchanged niobate layer perovskites, have low loss at all frequencies. Techniques were developed to eliminate ions from the thin films by burnout of organic components and dehydration/condensation reactions. This reaction scheme is illustrated in Figure 2.

*Surface sol-gel synthesis of titanate and tantalate thin films.* A layer-by-layer sol-gel process was developed for growing high dielectric Ti-Ta oxide ultrathin films. Patterned arrays of 1-10 nm thick oxides have been made by combining this sol-gel technique with microcontact printing ( $\mu$ -CP). AFM and SEM images show that the films are smooth and free of cracks or pinholes. However, as grown they are less dense than the corresponding bulk oxides and do not adhere well to Si. Annealing at 400°C densifies the oxides and makes adherent thin films.

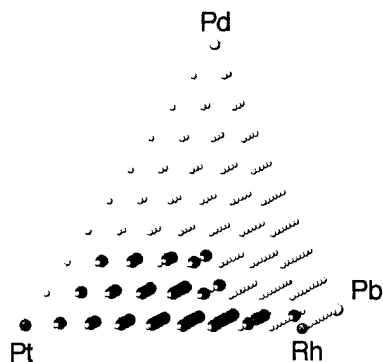
*Preparation of rod colloids by replication of porous membranes.* Rod colloids were made by electrochemical replication of porous alumina membranes. Monodisperse samples of "striped" and "tipped" 200 nm diameter Au/Pt rods are being studied as building blocks of three-dimensional woodpile architectures. The length of the individual segments (Au or Pt) can be controlled to  $\pm 10\%$  by controlling the electrodeposition time. Orthogonal self-assembly experiments have been done to show that the tips of Au-Pt-Au rods can be selectively derivatized with thiol-terminated fluorescent dyes, while the Pt barrels of the rods are rendered non-adhesive using a butylisocyanide monolayer. Electronic transport measurements on individual Au rods show that their conductivity is about one order of magnitude lower than bulk annealed Au. Current experiments, supported under the DARPA Moletronics program, focus on making Au/molecule/metal two-terminal devices, and on self-assembling rod arrays on lithographically patterned substrates by DNA hybridization.



**Figure 4.** Results of templated electrochemical growth of metal nanorods from porous alumina membranes. Top: Rod length is controlled coulometrically. Bottom: cylindrical rods with pre-determined stripe patterns are produced by sequentially plating different metals.

*Dynamic lattice gas simulations.* Extensive simulations have been performed of one-dimensional lattice models for dynamical geometries relevant to nano- and micro-scale chemical self-assembly. These simulations have demonstrated the evolution of structure. Mean-field analysis of the models has begun and is being compared with the numerical results. An asynchronous two dimensional model for particles interacting with a triangulated surface has been constructed, but not yet simulated.

*Combinatorial Discovery and Optimization of Sensor Materials.* Although not part of our original proposal, ARO's interest in chemical and biochemical sensors, and progress in our laboratory on combinatorial catalysis, motivated us to attempt to adapt combinatorial techniques to the discovery of better sensor materials. As a proof of concept example we prepared and screened 715-member pentanary alloy arrays for activity as glucose oxidation catalysts. Screening was carried out by converting the current at each electrode spot to a fluorescence signal, taking advantage of the fact that catalytic glucose oxidation lowers the local pH. Figure 5 shows an activity map of one of the quaternary regions scanned. The most active compositions contained both Pt and Pb, which means that these two elements play key roles in glucose oxidation. Bulk quantities of catalysts with compositions corresponding to those identified in the screening experiments were prepared and characterized. The best alloy electrocatalysts catalyzed glucose oxidation at substantially more negative potentials than pure platinum in enzyme-free voltammetric measurements. They were also insensitive to potential interferents (ascorbic and uric acids, and 4-acetamidophenol), which are oxidized at slightly more positive potentials. Rotating disk electrode (RDE) experiments were carried out to study the catalytic mechanism. The improvement in catalytic performance was attributed to the inhibition of adsorption of oxidation products, such as gluconolactone, which poison Pt electrodes.



**Figure 5.** Activity map in the Pd-Pt-Rh-Pb composition space for electrocatalytic glucose oxidation. The most active catalysts are found near the Pt-Rh-Pb ternary face of the map.

## **Publications**

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Y. Sun, H. Buck, and T. E. Mallouk, "Combinatorial Discovery of Alloy Electrocatalysts for Amperometric Glucose Sensors," submitted to *J. Am. Chem. Soc.*

## **Personnel Report**

August 1996-May 2000

<b><u>Name</u></b>	<b><u>Role in Project</u></b>	<b><u>Period of Support</u></b>	<b><u>Degree Awarded</u></b>
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Fang, Mingming	Postdoc	Jun. 1996-Jun. 1997; Oct. 1997-May 1998	
Hasslacher, Brosl	Co-PI	Aug. 1996-Sept. 1998	
He, Enfei	Postdoc	Jan.-May 1999	
Kaschak, David	GSRA	Aug. 1996-May 1997	Ph.D. 1998
Mallouk, Thomas	PI	Aug. 1996-Apr. 1997; July-Aug. 1998	
Martin, Benjamin	GSRA	Oct. 1997-Dec. 1998	
Meyer, David	Co-PI	Aug. 1996-Sept. 1998	
Ollivier, Patricia	GSRA	Aug. 1996-May 1997	Ph.D. 1998
Raker, Joseph	GSRA	Jan.-May 1999	
St. Angelo, Sarah	GSRA	Jan.-May 1999	
Sun, Yipeng	Postdoc	Jan.-May 2000	
Yu, Jong-Sung	Postdoc	May 1998; Aug. 1998 - May 1999	

**Inventions**

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T. E. Mallouk, H. Buck, and Y. Sun, "Combinatorial Discovery of Improved Alloy Electrocatalysts for Amperometric Glucose Sensors," Penn State University Invention Disclosure 2000-2295, U. S. Provisional Patent filed June, 2000.